240. *Vibrational Frequency Correlations in Heterocyclic Molecules. Part IV.*[1] *Indoxyl Derivatives.*

By S. J. Holt, A. E. Kellie, D. G. O'Sullivan, and P. W. Sadler.

Infrared spectra of *N*-methylindoxyl, thioindoxyl, and a series of substituted *N*-acetylindoxyls indicate that they all possess fully ketonic structures in the solid, in chloroform, and in carbon disulphide. Consequently, hydrogen bonding is absent from these compounds, but weak hydrogen-bonded association occurs in substituted *O*-acetylindoxyls. The method involving study of the effect of ring substituents on carbonyl frequencies, and utilization of σ–ν correlations to assign bands, has been applied to series of *N*- and *O*-acetylindoxyls, diacetylindoxyls, *N*-acetyloxindoles, and *N*-acetylisatins. Double σ–ν correlation exists with *N*-acetylindoxyls. Diacetylindoxyls provide good single correlation, but the substituent effects on the ester carbonyl frequencies in these compounds and in *O*-acetylindoxyls, after transmission through an indole ring and an oxygen atom, are not linearly related to σ values. These correlations indicate frequency assignments. No evidence of σ-correlations was observed with *N*-acetylisatins, but comparison with isatins permits tentative band assignments for these compounds and for *N*-acetyloxindoles. The infrared results conclusively confirm the accepted formulæ for the *N*- and *O*-acetylindoxyls.

In previous Parts [1-3] investigations were made of carbonyl frequencies of certain bicyclic compounds in which the second ring possessed negligible aromatic character. Substituent effects were those of substituted benzenes. Here attention is devoted to indoxyl derivatives and, although many of the compounds studied are effectively substituted benzenes, *O*-acetylindoxyls possessing the indole ring-system probably exhibit more complex substituent effects. Unfortunately, it has not been possible to determine the infrared spectra of indoxyls themselves, and consequently no further light has been shed on their tautomeric structures and ease of oxidation to corresponding indigos. Apart from the investigation of tautomeric and hydrogen-bonded structures, substituent effects, and band assignment, infrared study of *N*- and *O*-acetylindoxyls was desirable to confirm the usually accepted structures of these two sets of compounds. This verification is of some importance in

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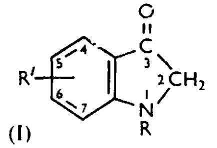
[1] Part III, O'Sullivan and Sadler, *J.*, 1957, 2916.
[2] *Idem, J.*, 1956, 2202.
[3] Kellie, O'Sullivan, and Sadler, *J.*, 1956, 3809.

view of the use of the *O*-acetyl derivatives as stain-producing substrates for the cytochemical localization of esterases in tissues and cells.[4]

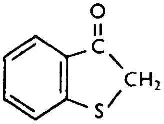
RESULTS AND DISCUSSION

(a) *Structures and Hydrogen Bonding.*—1-Methylindoxyl (I; R = Me, R′ = H), 1-acetylindoxyl (I; R = Ac, R′ = H), and thioindoxyl (II) might possess enolic structures, but the complete absence of absorption in the 3 μ region in the solid in chloroform and in carbon disulphide indicates that the compounds exist in the fully ketonic form. Indeed, no strong absorption occurs at greater frequencies than the intense carbonyl stretching maxima near 1750 cm.$^{-1}$; even the CH stretching frequency is of very low intensity. This not only confirms the ketonic structures but, taken in conjunction with the existence of NH absorption in indoxyl acetates, proves conclusively that the *N*- and *O*-acetylindoxyls have been assigned the correct structures. Substituents (F, Cl, Br, I, Me, MeO) in the 1-acetylindoxyl molecule (I; R = Ac) do not radically alter its absorption pattern, confirming the ketonic structure of these compounds previously indicated by such chemical behaviour as ready formation of oximes and semicarbazones. As the 1-acetyl compounds and thioindoxyl exist in their keto-forms, hydrogen bonding cannot occur, but their relatively high melting points indicate high lattice energies arising possibly from dipolar association. However, substituted indoxyl acetates (III; R = H, R′ = H, F, Cl, Br, I, Me, MeO, CF_3; R″ = Ac) possess intermolecular CO • • • HN links, producing broad bands with maxima between 3340 and 3270 cm.$^{-1}$.

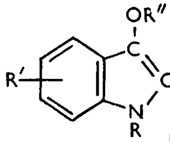
(b) *Band Assignments for Indoxyl Acetates.*—The NH stretching frequencies between 3340 and 3270 cm.$^{-1}$ are typical of heterocyclic imines participating in weak CO • • • HN bonding,[2, 3, 5] but the additional sharp peaks near 3450 cm.$^{-1}$ in oxindoles [3] and isatins [2] are absent. 1-Methylindoxyl acetate and 1-acetylindoxyl naturally show no NH absorption, and overtones [6] which sometimes exist are absent from this region. The carbonyl stretching frequencies are near 1740 cm.$^{-1}$. Absorption at about 1620 cm.$^{-1}$ is produced by CC stretching vibrations of the benzene ring.[7] In the 4- and 6-substituted compounds this band has half the carbonyl intensity but it is weak in other derivatives. The band just below 1500 cm.$^{-1}$ is also a benzene ring vibration,[8] and that near 1560 cm.$^{-1}$, absent from the 1-methyl and 1-acetyl compounds, is the NH deformation mode.



(I)



(II)



(III)

Probable assignments for the remaining bands in Table 1 are as follows: 1440 and 1370 cm.$^{-1}$ regions (methyl bending modes), strong band near 1340 cm.$^{-1}$ (Ph–N stretching vibration), intense absorption near 1220 cm.$^{-1}$ (C–O–C stretching frequency) [9] accompanied by slightly less intense maxima near 1080 and 910 cm.$^{-1}$ (other ester vibrations), strong absorption in the 820—780 cm.$^{-1}$ segment (out-of-plane bending motions in 1 : 2 : 3- or 1 : 2 : 4-trisubstituted aromatic ring).[10] The acetate band of 7-trifluoromethylindoxyl

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[4] Holt, *J. Histochem. Cytochem.*, 1956, **4**, 548.

[5] Sutherland, *Discuss. Faraday Soc.*, 1950, **9**, 274; Richards and Thompson, *J.*, 1947, 1248; Witkop, *J. Amer. Chem. Soc.*, 1950, **72**, 614; Witkop and Patrick, *ibid.*, 1951, **73**, 1558; Darmon and Sutherland, *Nature*, 1949, **164**, 440.

[6] Letaur and Gropp, *J. Chem. Phys.*, 1953, **21**, 1621.

[7] Colthup, *J. Opt. Soc. Amer.*, 1950, **40**, 397.

[8] Bornstein, *Analyt. Chem.*, 1953, **25**, 512.

[9] Thompson and Torkington, *J.*, 1945, 640.

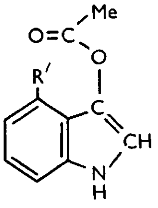
[10] McCauley, Lien, and Launer, *J. Amer. Chem. Soc.*, 1954, **76**, 2354.

acetate is complicated by the CF stretching frequencies which fall in this region and probably give rise to the 1260 and 1240 cm.$^{-1}$ maxima.

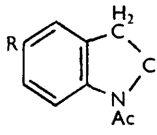
TABLE 1. *Frequencies of indoxyl acetates in potassium bromide discs.*

Subst.	Frequencies (cm.$^{-1}$)											
4-Cl	781	908	1048	1220	1330	1373	1435	1496	1577	1618	1741	3290
5-Cl	804	896	1093	1220	1344	1373	1436	1473	1550	1618	1740	3330
6-Cl	804	910	1078	1220	1336	1370	1456	1483	1580	1620	1742	3270
7-Cl	785	915	1095	1226	1344	1373	1446	1500	1550	1620	1735	3280
5-Me	800	911	1097	1223	1347	1371	1430	1495	1550	1617	1739	3340
5-Br	800	910	1083	1227	1340	1374	1428	1465	1548	1620	1740	3300
7-CF_3	802	928	1096	1200 1240 1260	1321	1370	1438	1467	1555	1620	1730	3320
4-Cl, 5-Br	796	910	1095	1223	1331	1367	1430	1460	1566	1603	1740	3280
None	814	910	1072	1225	1351	1372	1431	1462 1493	1550	1620	1743	3320
1-Me	801	900	1026	1230	1343	1375	1434	1477	—	1614	1733	—
Compd.												
N-Acetylindoxyl	764	—	—	—	1357	1388	1421	1466	—	1607	1674 1716	—

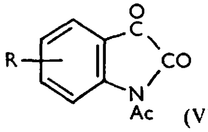
(c) *Carbonyl Stretching Frequencies of Indoxyl Acetates.*—Usual solvent effects are discernible in Table 2, the carbonyl frequencies being highest in carbon disulphide, significantly lower in the more polar chloroform, and, in general, slightly lower in the solid state, but here the shifts are more erratic. The effect of substituents is complex but frequency shifts are small and show a very rough tendency to increase with the Hammett σ values [11] of substituents in view of their location with reference to position 3 (σ_{Ph-O}). A linear relation between carbonyl frequencies and σ values is not to be expected as this system is not a simple substituted benzene, the substituent effects being transmitted first through the indole ring system and then through an oxygen atom. There is little consistency in the individual substituent effects in the two solvents (Table 2) and only very rough correspondence with substituent effects on the corresponding carbonyl frequencies in diacetylindoxyls (Table 3). Substitution at the imino-group has little influence on the carbonyl frequency (1-methyl-, 1-benzyl-, 1-carboxymethyl-, and the unsubstituted compound possessing maxima in chloroform at 1737, 1738, 1736, and 1738 cm.$^{-1}$ respectively), but extension of the ester side-chain appears to raise the frequency slightly (the acetate, propionate, and butyrate showing maxima in chloroform at 1738, 1744, and 1745 cm.$^{-1}$ respectively).



(IV)



(V)



(VI)

Usually, as the carbonyl stretching frequency of an acetate increases, the C–O–C frequency diminishes. Table 2 shows that this is not a general feature of indoxyl acetates, being exhibited only by the series 1-methylindoxyl, indoxyl, and thioindoxyl acetates. An interesting feature displayed in Table 2 is the splitting of the CO and C–O–C frequencies in the 4-substituted compounds in carbon disulphide. A likely explanation depends on the assumption that two preferred positions exist for the acetate side-chain. In one of

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[11] Hammett, " Physical Organic Chemistry," McGraw-Hill, New York, 1940, p. 188; Jaffé, *Chem. Rev.*, 1953, **53**, 191.

these positions (IV), the double-bond character of the carbonyl group is increased by a field effect produced by the propinquity of the 4-substituent.[12]

(d) *Carbonyl Stretching Frequencies of Diacetyl- and* 1-*Acetyl-indoxyls*.—In diacetylindoxyl (III; R = R″ = Ac, R′ = H), one carbonyl group has a position similar to that in acetanilide, and hence substituents in the benzene ring should exert a fairly marked effect on the stretching frequency of this carbonyl group, the frequency shifts being linearly

TABLE 2. *σ-Values and* C–O–C *and* CO *stretching frequencies* (*cm.*$^{-1}$) *of indoxyl acetates.*

			ν(C–O–C)		ν(CO)		
Indoxyl acetate	M. p.	$\sigma_{\text{Ph–O}}$	*a*	*c*	*a*	*b*	*c*
4-Cl, 5-Br-	107°	—	1223	1199 1218	1740	1750	1745 1778
4 : 5-Cl_2-	95	—	—	1201 1217	—	1746	1745 1777
4-I-	216	—	—	1192 1222	—	—	1741 1768
4-Cl-	86	—	1220	1194 1220	1741	1747	1745 1780
4-Br-	107	—	—	1191 1225	—	1744	1743 1770
7-CF_3-	95	0·415	1200	1204	1730	1742	1758
5-Br-	134	0·391	1227	1213	1740	1742	1746
7-Cl-	125	0·373	1220	1220	1740	1740	1746
5-Cl-	86	0·373	1226	1199 1218	1736	1740	1747
5-I-	149	0·352	—	1207	—	1739	1747
7-I-	84	0·352	—	1197 1216	—	1741	1745
5-F-	140	0·337	—	1213	—	1740	1749
6-I-	224	0·276	—	1213	—	1740	1749
6-Br-	200	0·232	—	1213	—	—	1746
6-Cl-	106	0·227	1220	1213	1742	1742	1749
6-F-	138	0·062	—	1213	—	1744	1749
5-Me-	117	−0·069	1223	1215	1739	1736	1743
1-Me-	61	—	1223	1220	1740	1737	1742
Indoxyl esters							
Acetate	129	0·0	1225	1213	1743	1738	1743
Propionate	90	—	—	1223	—	1744	1745
Butyrate	93	—	—	—	—	1745	—
Benzoate	101	—	—	1223	—	—	1728
Thioindoxyl acetate	liq.	—	—	1201	—	—	1768

Data in columns *a*, *b*, and *c* have been obtained from (*a*) potassium bromide discs, (*b*) chloroform solutions, and (*c*) carbon disulphide solutions respectively. Where blanks occur in these columns, the frequencies have not been measured. All the bands quoted are intense.

TABLE 3. *σ-Values relative to* Ph–N *linkage and* CO *stretching frequencies* (*cm.*$^{-1}$) *of acetanilides, diacetylindoxyls, and* 1-*acetylindoxyls in chloroform.*

		Acetanilides [a]	Diacetylindoxyls			*N*-Acetylindoxyls		
Subst.	$\sigma_{\text{Ph–N}}$	ν(CO)	M. p.	ν_1(CO)	ν_3(CO)	M. p.	ν_1 (CO)	ν_3(CO)
5-NO_2	0·778	—	220°	1717	1763	—	—	—
6-NO_2	0·710	1696	195	1713	1757	—	—	—
4-Cl, 5-Br	0·600	—	167	1711	1756	177°	1685	1721
6-Br	0·391	—	123	1707	1752	187	1681	1714
4-Cl	0·373	—	128	1708	1753	190	1681	1716
6-Cl	0·373	1690	117	1707	1751	171	1680	1715
6-I	0·352	1690	124	1707	1750	190	1679	1715
5-I	0·276	—	133	1707	1754	200	1677	1718
5-Br	0·232	—	124	1706	1755	188	—	—
5-Cl	0·227	1688	130	1706	1755	163	1674	1719
6-MeO	0·115	1686	145	1702	1755	178	—	—
5-F	0·062	1685	142	1700	1751	148	1672	1716
None	0·0	1685	83	1700	1751	138	1673	1710
5-Me	−0·170	1682	106	1696	1750	156	1669	1705
5-MeO	−0·260	1678	100	1692	1745	170	1669	1703

[a] In relation to the data on substituted acetanilides,[13] position 5 refers to *para*-substitution and positions 4 and 6 to *meta*-substitution.

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[12] Bellamy, Thomas, and Williams, *J.*, 1956, 3704; Bellamy and Williams, *J.*, 1957, 861; Jones, Forbes, and Muller, *Canad. J. Chem.*, 1957, **35**, 504.

[13] O'Sullivan and Sadler, *J. Org. Chem.*, 1956, **21**, 1179.

related to the σ value of the substituent with reference to its position relative to the Ph–N linkage ($\sigma_{\text{Ph-N}}$). The other carbonyl group is analogous to that in indoxyl acetate and consequently ring substituents R′ should exert a smaller and more erratic effect. Substituted diacetylindoxyls each exhibit two carbonyl stretching frequencies, the lower being the more intense. Comparison of the frequencies with those of acetanilide and with the σ values in Tables 3 and 4 shows that the band near 1700 cm.$^{-1}$ is produced by the *N*-acetyl- and that near 1750 by the *O*-acetyl-carbonyl group. The best values for the 1700 cm.$^{-1}$ band frequencies are given by the regression line $\nu_1 = 1700 + 21{\cdot}4\sigma_{\text{Ph-N}}$, the correlation coefficient (r) being 0·984. Table 3 shows the absence of correlation between the 1750 cm.$^{-1}$ band frequencies of diacetylindoxyls and $\sigma_{\text{Ph-N}}$ values, but the existence of rough correlation with $\sigma_{\text{Ph-C}}$ values is demonstrated in Table 4.

TABLE 4. *σ-Values relative to* Ph–C *linkage and upper* CO *stretching frequencies of 1-acetylindoxyls and diacetylindoxyls in chloroform.*

Substituent	6-NO$_2$	5-NO$_2$	4-Cl, 5-Br	5-Br	5-Cl	5-I	5-F	4-Cl
$\sigma_{\text{Ph-C}}$	0·778	0·710	—	0·391	0·373	0·352	0·337	—
ν_3(CO) of *N*-acetylindoxyls	—	—	1721	—	1719	1718	1716	1716
ν_3(CO) of diacetylindoxyls	1757	1763	1756	1755	1755	1754	1751	1753

Substituent	6-I	6-Br	6-Cl	5-MeO	None	5-Me	6-MeO
$\sigma_{\text{Ph-C}}$	0·276	0·232	0·227	0·115	0·0	−0·069	−0·268
ν_3(CO) of *N*-acetylindoxyls	1715	1714	1715	1703	1710	1705	—
ν_3(CO) of diacetylindoxyls	1750	1752	1751	1745	1751	1750	1755

1-Acetylindoxyls provide a good example of the use of σ–ν correlations in assigning frequencies to the responsible groups. As shown with substituted isatins,[2, 3] an independent double correlation (cross correlation) can occur in the same molecule. Here the lower frequencies of 1-acetylindoxyls correlate well with the $\sigma_{\text{Ph-N}}$ values of the substituents (Table 3), and the frequencies of the band near 1715 cm.$^{-1}$ with $\sigma_{\text{Ph-N}}$ values (Table 4). The equations of the regression lines for the frequencies are

$$\nu_1 = 1673 + 19{\cdot}4\sigma_{\text{Ph-N}} \quad . \ . \ . \ . \ . \ . \ . \ . \ . \quad (1)$$

$$\nu_3 = 1708 + 26{\cdot}7\sigma_{\text{Ph-N}} \quad . \ . \ . \ . \ . \ . \ . \ . \ . \quad (2)$$

and the respective correlation coefficients are 0·966 and 0·972. It is clear from Table 4 that the 5-methoxy-group exerts an anomalous effect on the upper carbonyl frequency of 1-acetylindoxyl and probably a corresponding effect on diacetylindoxyl. The methoxy-group frequently behaves abnormally in σ-correlations and the figures for this group have been omitted in computing equation (2) and its correlation coefficient. Thus the ν_1 bands (Table 3 and equation 1) are produced by stretching vibrations of the *N*-acetyl carbonyl group, and the ν_3 bands (Tables 3, 4, and equation 2) are due to the carbonyl group in position 3.

(e) *Carbonyl Stretching Frequencies of Substituted* N-*Acetyloxindoles and* N-*Acetylisatins.*—An attempt has been made to glean information on the carbonyl bands of acetyloxindoles (V) and acetylisatins (VI). The former are of interest in view of coupling phenomena. Abramovitch [14] has shown that coupling is a common feature in diacyl- and diaroyl-amines possessing reasonable symmetry. Investigation of this feature in oxindoles is complicated by the fact that oxindole itself and some substituted oxindoles [3] possess two well-separated carbonyl bands. Unfortunately, difficulties were encountered in preparing acetyloxindoles, the formation of dyes and other by-products preventing purification of the acetyl derivatives except in three cases. Their carbonyl frequencies (Table 5) increase with

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[14] Abramovitch, *J.*, 1957, 1413.

$\sigma_{\text{Ph-N}}$ values of the substituents as expected, but the results, by themselves, provide no information on the presence or absence of coupling interaction.

N-Acetylisatins, being more readily prepared, were studied in the hope that a triple σ–ν correlation might be unravelled and further information on coupling emerge. These compounds possess the expected three carbonyl maxima (Table 5), but complex interactions spoil possible σ–ν correlations. However, the fundamental frequencies of acetylisatins should be well separated and, therefore, coupling is unlikely. Comparison of the stretching frequencies ν_2 and ν_3 of the α- and β-carbonyl groups of isatin with the carbonyl frequencies of *N*-acetylisatin and 1-acetyloxindole (Table 5) suggests that the bands near 1720, 1775, and 1740 cm.$^{-1}$ in *N*-acetylisatin arise from vibrations of the carbonyl groups in the *N*-acetyl group, and in positions 2 and 3 respectively. In the absence of other evidence, this comparison also suggests that coupled oscillation does not occur in 1-acetyloxindole and that again the lower frequency ν_1 may be referred to the *N*-acetyl group.

TABLE 5. *Carbonyl stretching frequencies (cm.$^{-1}$) of acetylated oxindoles and isatins in chloroform.*

Compound	M. p.	$\sigma_{\text{Ph-N}}$	ν_1	ν_2	ν_3
Isatin	200°	—	—	1755	1740
N-Acetyloxindoles					
5-Methyl-	120	−0·170	1708	1752	—
(Unsubst.)	126	0·0	1710	1755	—
5-Nitro-	159	0·778	1720	1762	—
N-Acetylisatins					
(Unsubst.)	143	—	1721	1775	1742
5-Methyl-	173	—	1720	1772	1735
5-Methoxy-	175	—	1718 (sh)	1770	1732
5-Bromo-	166	—	1725	1786	1745
4-Chloro-	167	—	1720 (sh)	1776	1730
6-Chloro-	182	—	1720 (sh)	1787	1740
4 : 5-Dichloro-	194	—	1722	1772	1745
6-Fluoro-	177	—	1721	1772	1738

EXPERIMENTAL

Spectra.—Compounds were examined consecutively, under identical conditions for each medium, a Perkin-Elmer 21 double-beam recording spectrometer fitted with a rock-salt prism being used.

Diacetylindoxyls.—These compounds were prepared by heating the corresponding substituted *o*-carboxylphenylglycines under reflux with acetic anhydride and anhydrous sodium acetate.[15] *Diacetyl-5-methoxyindoxyl* (Found: C, 62·9; H, 5·4; N, 6·3. $C_{13}H_{13}O_4N$ requires C, 63·2; H, 5·3; N, 6·7%) formed needles (from aqueous ethanol). *Diacetyl-6-methoxydindoxyl* (Found: C, 63·1; H, 5·3; N, 6·3%) was obtained as white plates from the same solvent.

Indoxyl Esters.—The acetates were obtained from the corresponding diacetylindoxyls by deacetylation, under nitrogen, with boiling aqueous alkali, followed by reacetylation with acetic anhydride under Schotten–Baumann conditions.[15] Indoxyl propionate, butyrate, and benzoate were similarly prepared.

1-Methylindoxyl acetate was obtained from *o*-carboxyphenyl-*N*-methylglycine and boiling acetic anhydride containing anhydrous sodium acetate.[16] In a similar manner (*o*-carboxyphenylthio)acetic acid gave thioindoxyl acetate.[15]

1-*Acetylindoxyls.*—To the corresponding diacetylindoxyl (0·1 g.), in the minimum volume of boiling ethanol, was added hydrated sodium sulphite (0·1 g.) in twice the volume of hot

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[15] Holt and Sadler, *Proc. Roy. Soc.*, 1958, *B* (in the press); Holt and Petrow, *J.*, 1947, 611; Schwartz, *Monatsh.*, 1905, **26**, 1253.

[16] Ettinger and Friedländer, *Ber.*, 1912, **45**, 2075.

water. The mixture was heated under reflux for 10 min. and cooled; the product crystallized from aqueous ethanol giving, in good yield, the appropriate 1-acetylindoxyl as white needles (see Table 6).

N-*Acetylisatins.*—Acetylation of isatins was effected by heating the solids under reflux for 1—2 hr. with excess of acetic anhydride.[17] Crude acetyl derivatives, which separated from the cooled mixtures, were purified by crystallization from acetic acid (charcoal) (see Table 7). 7-Chloro- and 7-nitro-isatin could not be acetylated by this procedure, presumably owing to steric hindrance. M. p.s of 1-acetyl-isatins and -oxindoles are in Table 5.

TABLE 6. N-*Acetylindoxyls.*

		Found (%)			Required (%)	
	M. p.	C	H	Formula	C	H
5-*Fluoro-*	148°	62·0	4·6	$C_{10}H_8O_2NF$	62·2	4·2
4-*Chloro-*	190	57·2	3·6	$C_{10}H_8O_2NCl$	57·3	3·8
5-*Chloro-*	163	57·4	4·0	$C_{10}H_8O_2NCl$	57·3	3·8
6-*Chloro-*	171	57·5	4·0	$C_{10}H_8O_2NCl$	57·3	3·8
7-*Chloro-*	191	57·1	4·1	$C_{10}H_8O_2NCl$	57·3	3·8
6-*Bromo-*	187	47·7	3·5	$C_{10}H_8O_2NBr$	47·3	3·2
6-*Iodo-*	190	40·2	3·0	$C_{10}H_8O_2NI$	39·9	2·7
5-*Bromo*-4-*chloro-*	177	41·9	2·4	$C_{10}H_7O_2NBrCl$	41·6	2·4
5-*Methyl-*	156	69·8	5·6	$C_{11}H_{11}O_2N$	69·9	5·8
6-*Methoxy-*	178	64·1	5·3	$C_{11}H_{11}O_3N$	64·4	5·4

TABLE 7. N-*Acetylisatins.*

		Found (%)			Required (%)	
	Appearance	C	H	Formula	C	H
6-*Fluoro-*	Yellow needles	58·2	2·9	$C_{10}H_6O_3NF$	58·0	2·9
4-*Chloro-*	Yellow needles	53·9	3·0	$C_{10}H_6O_3NCl$	53·7	2·7
6-*Chloro-*	Yellow needles	53·9	2·6	$C_{10}H_6O_3NCl$	53·7	2·7
5-*Bromo-*	Orange plates	44·7	2·2	$C_{10}H_6O_3NBr$	44·8	2·3
4 : 5-*Dichloro-*	Thick yellow plates	46·8	1·8	$C_{10}H_5O_3NCl_2$	46·5	1·9
5-*Methyl-*	Orange needles	64·9	4·5	$C_{10}H_9O_3N$	65·0	4·5
5-*Methoxy-*	Yellow needles	59·8	4·4	$C_{11}H_9O_4N$	60·3	4·1

N-*Acetyloxindoles.*—Attempts were made to prepare a selection of *N*-acetyloxindoles by direct acetylation (Suida [18]) but, owing to dye-formation and other gross contamination, only two, in addition to the previously-described unsubstituted compound, were obtained pure. The 5-*methyl compound* (Found: C, 69·5; H, 5·9. $C_{11}H_{11}O_2N$ requires C, 69·8; H, 5·8%) was obtained as white needles from ethanol. Similar purification gave the 5-*nitro-compound*, also as white needles (Found: C, 54·5; H. 4·0. $C_{10}H_8O_4N_2$ requires C, 54·5; H, 3·7%).

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[17] Camps, *Arch. Pharm.*, 1899, **237**, 687.

[18] Suida, *Ber.*, 1879, **12**, 1327.